Theoretical and Experimental Investigation on Dipole Moment of Synthetized y_t-Base in the Ground and Excited States*

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The electric dipole moment of y_t-Base calculated by the CNDO/S and JNDO/S method is $\mu_g = 3.42$ D and $\mu_g = 3.74$ D in the ground state and $\mu_e = 4.41$ D and $\mu_e = 5.67$ D in the first excited $\pi\pi^*$-state, respectively, μ_g and μ_e being nearly antiparallel. Measurements of absorption and fluorescence spectra of y_t-Base in aprotic solvents of different polarity yielded $\mu_g = 3.8$ D and $\mu_e = 4.3$ D and the directions of dipole moments were found to be nearly antiparallel.

This comparison may be considered as an indication for the $\pi\pi^*$ character of the observable first excited state, although the CNDO/S- and JNDO/S-calculations predict a $n\pi^*$-state as the lowest lying excited state.

1. Introduction

In the last few years several experimental and quantum chemical investigations on the electronic properties of the y_t-Base (Fig. 1) were published [1]. The comparisons between the experimentally determined and quantum chemically calculated values were limited to the transition energies and intensities. However, it is well known that it is possible to get changes in the sequence of close lying states, already with small changes in the parametrization of the quantum chemical calculation. In such cases other properties, such as charge densities and dipole moments should be used as criteria, if the states show remarkable differences in this regard. In general, these properties do not change so drastically with the parametrization.

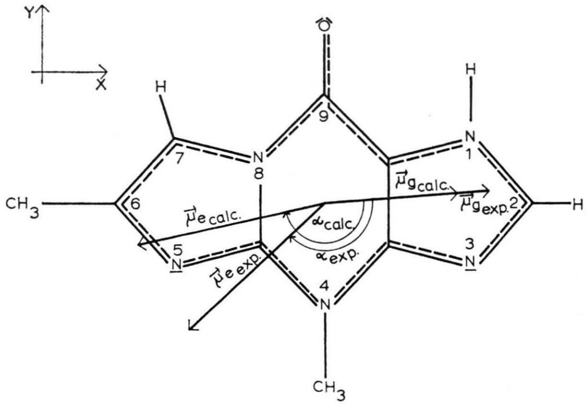

Fig. 1. y_t-Base with calculated (CNDO/S) and -experimentally determined dipole moments.

It was the aim of the present work to get further information about the electronic properties of the ground and singlet excited states by comparison of their experimentally determined and quantum chemically calculated dipole moments.

The CNDO/S- and JNDO/S-methods (*c*omplete/*i*ntermediate *n*eglect of *d*ifferential *o*verlap) are suitable for the calculations if the configuration interaction includes enough orbitals. It may be that the 60 configurations currently used [1] do not meet this requirement.

Two different experimental methods were used for the determination from solvent shifts of the electronic spectra of the dipole moments in the ground (μ_g) and first excited singlet (μ_e) states, and of the angle between them. Furthermore, the use of aprotic solvents of different polarities helped to detect the different electronic states in the observed absorption bands.

2. Methods of Quantum Chemical Calculations

The CNDO/S- and JNDO/S-methods were employed with the parametrization of Ellis et al. [2]. The Mataga-Nishimoto approximation [3] and (for JNDO/S) the one-centre parameters G_1 and F_2 from Pople and Beveridge [4] were used. The configuration interaction included 90 configurations:

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The lowest five unoccupied π^*-orbitals and all occupied π-, n- and σ-orbitals down to the deepest n- or π-orbital. This was necessary because we observed considerable mixing between the $n \rightarrow \pi^*$- and $\sigma \rightarrow \pi^*$-excitations in preliminary calculations on the y_t-Base without methyl groups. The results show that the methyl groups substantially influence the dipole moments, and these groups intensify the mixing mentioned above.

The structure was taken from the single-crystal X-ray diffraction data [5], but the π-system was then planarized (according to minimum changes in bond lengths the bond angles were changed) to ensure the invariance of the CNDO/S- and JNDO/s-results (factor 0.585 for $\beta_{\pi\pi}$-resonance integrals only).

The dipole moments were obtained from the equation [4]

$$\boldsymbol{\mu}_\mathrm{i} = \sum_{\mathrm{A}}^{\text{(all atoms)}} \left\{ 4.803\,(Z_\mathrm{A}' - P_\mathrm{AA})\, \boldsymbol{i}_\mathrm{A} - 7.337\, \frac{P_\mathrm{A}(2\mathrm{s}, 2\mathrm{p_i})}{\xi_\mathrm{A}} \cdot \frac{\boldsymbol{i}_\mathrm{A}}{|\boldsymbol{i}|} \right\} \quad (1)$$

with ξ_A the Slater-Exponent, Z_A' the core charge and P_AA, $P_\mathrm{A}(2\mathrm{s}, 2\mathrm{p_i})$ the atomic charge densities and the elements of the charge-bond-order matrix.

The convergence limit for the energy in the SCF-calculations was 10^{-4} eV.

3. Synthesis and Purification of y_t-Base

The y_t-Base was synthetized by direct condensation of 3-methylguanin with brom-acetone according to Kasai et al. [6]. Twofold recrystalization from water or methanol yielded a chromatographically pure product.

4. Determination of Electric Dipole Moments from Absorption and Fluorescence Spectra

Absorption spectra were measured on a Beckman Model 25 and Specord (VEB Carl Zeiss, Jena) spectrophotometers. The arrangement for the fluorescence measurements has been described in our previous paper [7]. The solvents used were of spectroscopical grade or p.a.

From the theory of the solvent dependence of electronic spectra [8, 9] we have the following equations:

Difference between the wavenumbers of the absorption ($\tilde{\nu}_\mathrm{A}$) and fluorescence ($\tilde{\nu}_\mathrm{F}$) maxima:

$$\tilde{\nu}_\mathrm{A} - \tilde{\nu}_\mathrm{F} = m_1 f(\varepsilon, n) + \text{const.}, \quad (2)$$

where

$$m_1 = \frac{2(\boldsymbol{\mu}_\mathrm{e} - \boldsymbol{\mu}_\mathrm{g})^2}{h c a^3} \quad (3)$$

and

$$f(\varepsilon, n) = \frac{2n^2+1}{n^2+2} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right). \quad (4)$$

Shift of the fluorescence maximum:

$$-\tilde{\nu}_\mathrm{F} - m_1 \frac{f(\varepsilon, n)}{2} = m_2 \left[\frac{f(\varepsilon, n)}{2} + g(n) \right] + \text{const.}, \quad (5)$$

where

$$m_2 = \frac{2(\mu_\mathrm{e}^2 - \mu_\mathrm{g}^2)}{h c a^3} \quad (6)$$

and

$$g(n) = \frac{3}{2} \frac{n^4 - 1}{(n^2 + 2)^2}. \quad (7)$$

ε and n are the dielectric constant and the refractive index of the solvent, respectively, h is Planck's constant, c the velocity of light and a the Onsager cavity radius.

The angle α between the vectors $\boldsymbol{\mu}_\mathrm{e}$ and $\boldsymbol{\mu}_\mathrm{g}$ can be evaluated by solving the Eqs. (3) and (6).

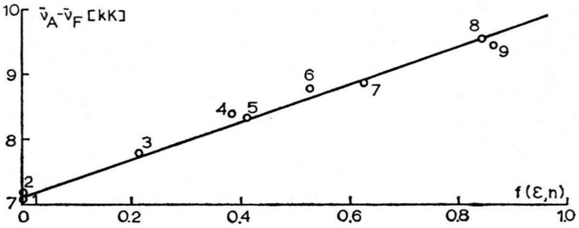

Fig. 2. Stokes shift of the y_t-Base (solvents: 1-cyclohexane with 0.2% methanol, 2-benzene, 3-trichlorethylene, 4-diethylether, 5-butylacetat, 6-tetrahydrofuran, 7-1,2-dichlorethane, 8-N,N'-dimethylformamid, 9-acetonitril).

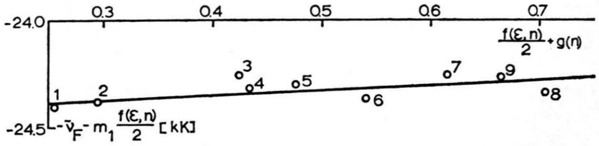

Fig. 3. Fluorescence maxima corrected by $m_1(f(\varepsilon, n)/2)$ (see Eq. (5)) of the y_t-Base in various solvents (see Figure 2).

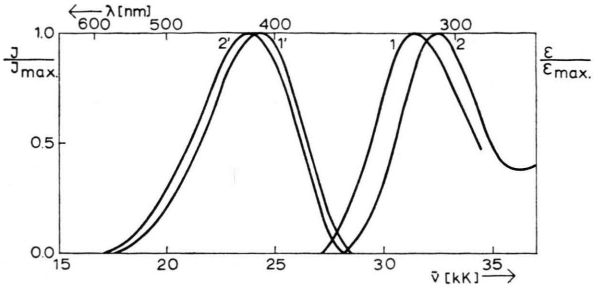

Fig. 4. Normalized absorption and fluorescence spectra of the y_t-Base (1,1′-in trichlorethylene, 2,2′-in N,N′-dimethylformamide).

From Eqs. (3) and (6) we can determine μ_e and α if μ_g is known from another method. The empirical parameters m_1 and m_2 are the slopes of the straight lines shown in Figs. 2 and 3. The value of μ_g was evaluated on the basis of the Gorodyskii-Bakhshiev theory [10, 11].

The solvents used were dimethylformamide ($\mu_s = 3.86$ D, $a_s = (3.3 \div 3.4)$ Å, $\varepsilon = 38.6$) and trichlorethylene ($\mu_s = 0.94$ D, $a_s = (2.8 \div 2.9)$ Å, $\varepsilon = 3.42$). Two examples of the spectra are shown in Figure 4.

On the basis of the structure [5] and the interaction radii of the atoms the Onsager cavity radius for the y_t-Base was estimated to be 5.8 Å. This value was then used in Eqs. (3) and (6).

5. Results and Discussion

The calculated and observed transition energies, and the relative oscillator strengths and intensities are shown in Table 1. The whole absorption spectrum may be divided into three bands as indicated in this Table.

Both calculations predict the $n\pi^*$-state as the first and the $\pi\pi^*$-state of weak intensity as the second excited singlet state, these together forming the first band. No indications for this hidden $n\pi^*$-state were found from the absorption and fluorescence spectra in different solvents (see for example Figure 4). This n-orbital according to the CNDO/S-results is mainly localized at the oxygen atom, and according to the JNDO/S-results at the nitrogen N_3 (Fig. 1) as well as at the oxygen atom.

Both methods predict changes of the electronic density at the nitrogen sites 3 and 5 (Fig. 1) for the two transitions from the ground state. The differences at these atoms are small and the experimentally determined change of the pK_s-values for the ground and excited state are not very large either [12].

Two features of the second and the third band in the absorption spectra in solvents of different polarity confirm the calculated description of these bands as being composed of several electronic states:

a) The third band in polar solvents (acetonitrile for instance), nearly symmetric and structureless, exhibits a new band in cyclohexane at the longwave side. This may be due to the splitting of this band into two transitions of distinct intensities.

b) The second band in polar solvents showing vibrationlike structure of two distinct (and

Table 1. Computed and observed transition energies [k K], relative intensities and classification of the electronic transition.

No. i	$\tilde{\nu}_{cal}$		$\tilde{\nu}_{obs}$ [a]	f_i/f_2		$\varepsilon_{max}/\varepsilon^{max}_{S_1(\pi,\pi^*)}$	Type [b]
	JNDO/S	CNDO/S		JNDO/S	CNDO/S		
1	31.07	31.70		0.01	0.01		$n\pi^*$, $n_1 \rightarrow L$
2	33.41	34.73	31.50	1.00	1.00	1.00	$\pi\pi^*$, $H \rightarrow L$
3	35.93	36.74	36.90	0.18	0.62	1.14	$\pi\pi^*$, $H \rightarrow L+1$
4	36.95	41.73 [c]	38.40	0.07	0.12 [c]	1.07	$n\pi^*$, $n_1 \rightarrow L+1$
5	37.48		(39.60) [d]	0.11		—	$n\pi^*$, $n_2 \rightarrow L+2$
6	38.91	39.16	42.00	4.11	5.91	0.93	$\pi\pi^*$, $H-1 \rightarrow L$
7	41.18	42.14	43.10	2.27	2.27	4.57	$\pi\pi^*$, $\begin{pmatrix} H & \rightarrow L+1 \\ H-1 & \rightarrow L+2 \end{pmatrix}$

[a] From absorption spectra of the y_t-Base in cyclohexane + 0.2% methanol.

[b] H highest occupied, L lowest unoccupied π-orbital, n_i σ-orbitals which may be classified as n-orbitals.

[c] The one-centre exchange integrals in JNDO cause another mixing within the n-orbitals compared with CNDO.

[d] A hidden absorption band uncertain.

Table 2. Dipole moments calculated for several excited states in comparison with the dipole moment of the ground state.

No. i^a	Type	CNDO/S				α^b	JNDO/S				α^b
		μ_x	μ_y	μ	$\lvert \boldsymbol{\mu}_e - \boldsymbol{\mu}_g \rvert$		μ_x	μ_y	μ	$\lvert \boldsymbol{\mu}_e - \boldsymbol{\mu}_g \rvert$	
		in Debye					in Debye				
0	ground state	3.41	0.25	3.42	—	—	3.67	0.68	3.73	—	—
1	$n\pi^*$	2.34	3.92	4.57	3.82	305	2.47	4.38	5.02	3.89	310
2	$\pi\pi^*$	− 4.31	− 0.95	4.41	7.81	172	− 5.21	− 2.20	5.67	9.34	168
3	$\pi\pi^*$	− 3.38	0.52	3.43	6.80	193	− 0.59	0.84	1.03	3.08	115
6	$\pi\pi^*$	− 4.10	1.01	4.22	7.55	198	—	—	—	—	—

^{a} Numbering as in Table 1. — ^{b} Angle in ° between $\boldsymbol{\mu}_e$, $\boldsymbol{\mu}_g$ (see Figure 1).

Table 3. Dipole moments of the ground ($\boldsymbol{\mu}_g$) and first excited singlet ($\boldsymbol{\mu}_e$) states and the angle α between them.

m_1 [cm^{-1}] (Eq. (2))	m_2 [cm^{-1}] (Eq. (5))	μ_g From Gorodyskii Bakhshiev theory [10]	$\lvert \boldsymbol{\mu}_e - \boldsymbol{\mu}_g \rvert$ (Eq. (3))	μ_e (Eq. (6))	α (Eq. (3))
		in Debye			
2900	200	3.8 ± 0.2	7.5	4.3	142°

eventually one hidden) maxima with an intensity ratio $\varepsilon_2^{\max}/\varepsilon_3^{\max} \approx 0.82$, is shifted to long waves in cyclohexane. The intensity ratio is then $\varepsilon_2^{\max}/\varepsilon_3^{\max} \approx 1.07$.

The agreement concerning the first and second bands observed in cyclohexane is better for the JNDO/S-results. The CNDO/S-results agree better with the most intense third observed band.

The calculated and experimentally determined dipole moments are shown in Tables 2 and 3. The calculated μ_z-component was in all cases smaller than 0.2 D and therefore negligible. The comparison shows that the observed first excited singlet state should be assigned to the $\pi\pi^*$-state, corresponding to the second calculated excited singlet state (Table 1). Two experimental observations led to the conclusion that the dipole moment in this state is greater than in the ground state and shows an inverse direction:

a) Blue shift with increasing polarity in absorption (Fig. 4), and

b) Inverse (red) shift of the fluorescence with increasing polarity (Figure 4).

The values obtained from Eqs. (2)—(7) are listed in Table 3 and confirm these conclusions.

The calculated values presented in Table 2 predict a similar behaviour of the other excited states. Indeed, different but always red shifts of the three absorption bands with decreasing polarity have been observed (for example in acetonitrile and cyclohexane).

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